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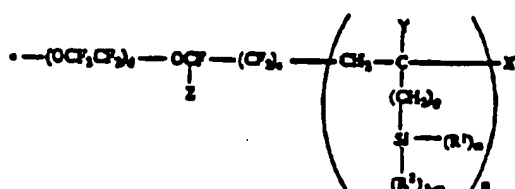
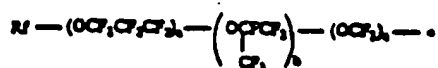
世界知的所有権機関
国際事務局
特許協力条約に基づいて公開された国際出願



<p>(51) 国際特許分類6 C08G 65/22, 65/32, C08L 71/02, C09D 5/16, 171/02</p>	<p>A1</p>	<p>(11) 国際公開番号 WO97/07155</p> <p>(43) 国際公開日 1997年2月27日 (27.02.97)</p>																																
<table border="0"> <tr> <td data-bbox="266 483 820 871"> <p>(21) 国際出願番号 PCT/JP96/02274</p> <p>(22) 国際出願日 1996年8月12日 (12.08.96)</p> <p>(30) 優先権データ</p> <table border="0"> <tr> <td>特願平7/227533</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/227534</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/227537</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279603</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279604</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279605</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平8/31392</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/31393</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/31394</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/71400</td> <td>1996年3月1日 (01.03.96)</td> <td>JP</td> </tr> </table> <p>(71) 出願人 (米国を除くすべての指定国について) ダイキン工業株式会社 (DAIKIN INDUSTRIES, LTD.) (JP/JP) 〒530 大阪府大阪市北区中崎西2丁目4番12号 梅田センタービル Osaka, (JP)</p> </td> <td data-bbox="820 483 1411 871"> <p>(72) 発明者: および (73) 発明者/出願人 (米国についてのみ) 田中勇次 (TANAKA, Yuji) (JP/JP) 蜂須賀仁治 (HACHISUKA, Hitoharu) (JP/JP) 荒瀬琢也 (ARASE, Takuya) (JP/JP) 根岸良夫 (NEGISHI, Yoshio) (JP/JP) 徳元正洋 (TATEMOTO, Masayoshi) (JP/JP) 清水哲男 (SHIMIZU, Tetsuo) (JP/JP) 山口貞亮 (YAMAGUCHI, Sadastaru) (JP/JP) 〒566 大阪府摂津市西一条1番1号 ダイキン工業株式会社 淀川製作所内 Osaka, (JP) 出崎全三 (DESAKI, Keizo) (JP/JP) 〒450 愛知県名古屋市中村区名駅南2丁目14番19号 住友生命名古屋ビル ダイキン工業株式会社 名古屋支店内 Aichi, (JP)</p> <p>(74) 代理人 弁理士 安富康男, 外 (YASUTOMI, Yasuo et al.) 〒532 大阪府大阪市淀川区西中島5丁目14番22号 リクルート新大阪ビル4階 Osaka, (JP)</p> <p>(81) 指定国 US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>添付公開書類 国際調査報告書</p> </td> </tr> </table>			<p>(21) 国際出願番号 PCT/JP96/02274</p> <p>(22) 国際出願日 1996年8月12日 (12.08.96)</p> <p>(30) 優先権データ</p> <table border="0"> <tr> <td>特願平7/227533</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/227534</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/227537</td> <td>1995年8月11日 (11.08.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279603</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279604</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平7/279605</td> <td>1995年10月2日 (02.10.95)</td> <td>JP</td> </tr> <tr> <td>特願平8/31392</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/31393</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/31394</td> <td>1996年1月24日 (24.01.96)</td> <td>JP</td> </tr> <tr> <td>特願平8/71400</td> <td>1996年3月1日 (01.03.96)</td> <td>JP</td> </tr> </table> <p>(71) 出願人 (米国を除くすべての指定国について) ダイキン工業株式会社 (DAIKIN INDUSTRIES, LTD.) (JP/JP) 〒530 大阪府大阪市北区中崎西2丁目4番12号 梅田センタービル Osaka, (JP)</p>	特願平7/227533	1995年8月11日 (11.08.95)	JP	特願平7/227534	1995年8月11日 (11.08.95)	JP	特願平7/227537	1995年8月11日 (11.08.95)	JP	特願平7/279603	1995年10月2日 (02.10.95)	JP	特願平7/279604	1995年10月2日 (02.10.95)	JP	特願平7/279605	1995年10月2日 (02.10.95)	JP	特願平8/31392	1996年1月24日 (24.01.96)	JP	特願平8/31393	1996年1月24日 (24.01.96)	JP	特願平8/31394	1996年1月24日 (24.01.96)	JP	特願平8/71400	1996年3月1日 (01.03.96)	JP	<p>(72) 発明者: および (73) 発明者/出願人 (米国についてのみ) 田中勇次 (TANAKA, Yuji) (JP/JP) 蜂須賀仁治 (HACHISUKA, Hitoharu) (JP/JP) 荒瀬琢也 (ARASE, Takuya) (JP/JP) 根岸良夫 (NEGISHI, Yoshio) (JP/JP) 徳元正洋 (TATEMOTO, Masayoshi) (JP/JP) 清水哲男 (SHIMIZU, Tetsuo) (JP/JP) 山口貞亮 (YAMAGUCHI, Sadastaru) (JP/JP) 〒566 大阪府摂津市西一条1番1号 ダイキン工業株式会社 淀川製作所内 Osaka, (JP) 出崎全三 (DESAKI, Keizo) (JP/JP) 〒450 愛知県名古屋市中村区名駅南2丁目14番19号 住友生命名古屋ビル ダイキン工業株式会社 名古屋支店内 Aichi, (JP)</p> <p>(74) 代理人 弁理士 安富康男, 外 (YASUTOMI, Yasuo et al.) 〒532 大阪府大阪市淀川区西中島5丁目14番22号 リクルート新大阪ビル4階 Osaka, (JP)</p> <p>(81) 指定国 US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>添付公開書類 国際調査報告書</p>
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<p>(54) Title: SILICON-CONTAINING ORGANIC FLUOROPOLYMERS AND USE OF THE SAME</p> <p>(54) 発明の名称 ケイ素含有有機含フッ素ポリマー及びその用途</p> <div style="text-align: center;"> $R^1 - (OCF_2CF_2CF_2)_a - \left(\begin{array}{c} OCF_2CF_2 \\ \\ CF_2 \end{array} \right)_b - (OCF_2)_c -$ $\cdot - (OCF_2CF_2)_d - OCF_2 - \left(\begin{array}{c} Z \\ \\ CF_2 \end{array} \right)_e - \left(\begin{array}{c} Y \\ \\ CH_2 \\ \\ Si - (R^2)_m \\ \\ (R^2)_n \end{array} \right)_f - X$ </div> <p>(57) Abstract</p> <p>Novel silicon-containing organic fluoropolymers which are applicable to materials over a wide range and have an excellent stain-proofness. The polymers are represented by general formula (I) and have a number-average molecular weight of from 5×10^3 to 10^5, wherein R^1 represents perfluoroalkyl; Z represents fluoro or trifluoromethyl; a, b, c, d and e independently represent each of 0 or an integer of 1 or above, provided that $a + b + c + d + e \geq 1$ and the order of the repeating units parenthesized with subscripts a, b, c, d, and e occurring in the formula is not restricted; Y represents hydrogen or C_{1-4} alkyl; X represents hydrogen, bromo or iodo; R^2 represents hydroxy or a hydrolyzable substituent; R^2 represents hydrogen or a monovalent hydrocarbon group; l is 0, 1 or 2; m is 1, 2 or 3 and n is an integer of 2 or above.</p>																																		

(54) Title: Silicon-Containing Organic Fluoropolymers and Use of th Same [English]

(54) Title of the Invention: Silicon-Containing Organic Fluoropolymers and Uses Thereof [Japanese]



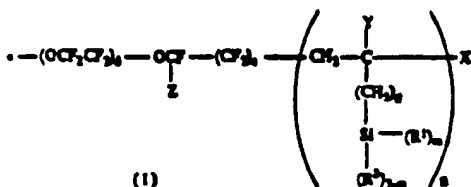
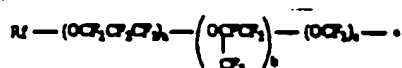
(I)

(57) Abstract

[insert English abstract]

(57) Abstract [Japanese version]

This invention has the objective of providing novel silicon-containing fluoropolymers applicable to a wide range of materials and which are of superior resistance to staining. The silicon-containing fluoropolymers of this invention are represented by general formula (I)



(I)

[wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, f indicates 0, 1 or 2, m indicates 1, 2 or 3 and n indicates an integer of 2 or greater] and have number average molecular weights of 5 x 10³ to 1 x 10⁵

Specification

Silicon-Containing Organic Fluoropolymers and Uses Thereof

Technological Field

This invention relates to novel silicon-containing organic fluoropolymers that have not been described in the literature and to the uses thereof. In further detail, it relates to silicon-containing organic fluoropolymers of superior solvent resistance and resistance to chemicals and that are effective in preventing staining on the surfaces of various types of base materials and to the uses thereof.

Background Technology

It is known that various organic fluoropolymers comprised of perfluoropolyethers exhibit superior heat resistance and resistance to chemicals as well as unique functions such as water and oil repellency and low refractive indices and they are known as polymers having an extremely wide range of use and high added value.

On the other hand, compounds having silane moieties as indicated by the general formula $\text{BSi(R)}_r\text{D}$, [wherein, B is an organic residue that can react with organic compounds such as polymers, D is a halogen or an alkoxy group, R is an alkyl group and r indicates 1, 2 or 3] are generally known as silane coupling agents and can be used as surface treatment agents of base materials. It is further known that polymers having them in their terminals can be hydrolyzed by water at room temperature and subjected to condensation polymerization and that they bring about cross-linking reactions, with hardening being effected [Encyclopedia of Chemical and Technology [sic], Vol. 12, pp. 464-569, 1970].

It is also known that attempts have been made to apply silane coupling agents to organic fluoropolymers, for example, fluorosilicones, copolymers of fluoroolefins and vinyl silanes and α , ω -bis (dialkylchlorosilyl) perfluoroalkanes [J. Polym. Sci., Part-A, Vol. 10, No. 3, pp. 947-953].

to get → Organic fluoropolymers containing vinyl silane compounds of this kind are disclosed in Japanese Patent Application Early Disclosure No. 1-294709 [1989]. Because these substances exhibit water repellency and resistance to staining, they can be used effectively, for example, for automobile exterior trim and paints.

Silicon compounds containing fluorine are disclosed in Japanese Patent Application Early Disclosure No. 5-339007 [1993] as examples of the application of this type of silane compound to organic fluoropolymers. These substances are characterized in that they have structures in which the aforementioned silane compounds are contained in perfluoropolyethers of organic fluoropolymers and in that they contain iodine with carbons bonded to said silane compounds. Because these substances have low surface energy, they can be applied as raw materials for fiber treatment agents, releasing agents and soiling preventive coating agents.

However, organic fluoropolymers containing silicon compounds that have been known up to the present contain only one reactive silicon atom in their terminals so that their soiling preventive capacity is insufficient. The term soiling preventive capacity refers to the property that dirt is not easily attached and to the property that attached dirt is easily eliminated by washing.

Base materials such as metals, glass and resins are commonly used in automobile parts, OA equipment and household electrical products. Dirt that is floating inside automobiles, inside offices and indoors and oleaginous substances that are mixed in food products and machine oils and that are difficult to wipe off become attached to the surfaces of these base materials and they are also soiled by fingerprints during use, for which reason a means is necessary so that these stains do not become readily attached and for preventing staining so that stains, once they become attached, can easily be removed.

A technology is disclosed in Japanese Patent Application Early Disclosure No.1-126244 [1989] as a treatment measure for preventing staining of glass surfaces in which polymeric substances such as polydimethylsiloxane are applied directly to glass surfaces or in which a paint film is formed by immersing the surface in the treatment agent. A technology is also known whereby chemically adsorbed monomolecular films containing fluorine are formed by chemical adsorption methods.

A technology is disclosed in Japanese Patent Disclosure No.7-53913 [1995] as a treatment measure for preventing staining of metal surfaces associated with organic composite plated steel plates in which a chromate coating comprised of a silica sol silane coupling agent is compounded in the top layer of a zinc plated coating and in which a thin film coating is formed on this top layer using an isocyanate paint composition.

However, there is not sufficient stain preventing capacity against oleaginous staining substances with these types of conventional treatment measures. There is also the problem that fingerprints easily become attached to the surfaces of base materials that are touched by the fingers and are difficult to remove.

Further, the effect is markedly decreased under the harsh conditions of outdoor exposure and is insufficient in respect to weather resistance. Moreover, expensive organic solvents containing fluorine must be used, for which reason there is a problem in terms of production costs.

On the other hand, the surfaces of base materials that are used for moving objects including vehicles such as automobiles and trains, aircraft and ships and for structures such as houses are exposed to wind and rain during use. In regions of cold and snow, they are in contact for long periods with snow and ice during winter. In addition, in special facilities such as ice-cooled test installations and in household products such as refrigerators, some of the parts are exposed to extremely low temperatures and the water in water droplets and air becomes attached to the ice.

When ice becomes attached to base materials of vehicles, it impairs their function. For example, in the case of windshields, accidents are caused as a result of vision being impeded. When ice becomes attached to parts of refrigerators, cooling efficiency is decreased and electric power is consumed and wasted.

A technology is disclosed in Japanese Patent Application Early Disclosure No.3-158794 [1991] whereby anti-clouding treatment is performed by forming a hydrophilic film.

A technology is disclosed in Japanese Patent Application Early Disclosure No.1-126244 [1991] whereby a film is formed and water repellency is achieved by applying an organic silicone compound such as a polydimethylsiloxane directly to a glass surface or by immersing the surface in a treatment agent.

Technologies are disclosed in Japanese Patent Application Early Disclosure No.4-338147 [1992] and in Japanese Patent Disclosure No.63-24554 [1988] whereby water repellency is obtained by forming a silicon oxide film containing fluoroalkyl groups on a glass surface by the chemical adsorption method or the sol gel method using fluoroalkyl silane compounds.

However, attachment of ice cannot be prevented effectively with anti-clouding treatments by forming a water repellent film. Further, with methods in which films of organic silicone compounds are formed on glass surfaces, these films do not become bonded chemically with the glass, for which reason there is a high possibility that the films will peel off during use. Thus, they are not of sufficient durability. Moreover, with methods in which films of silicon oxide containing fluoroalkyl groups are formed on glass surfaces, there is sufficient durability but lubricity is not sufficient. Even when these technologies are used individually or in combinations and even when water repellency is obtained, attachment of ice cannot be effectively prevented.

In the case in which attachment of ice is to be prevented, it is necessary either that ice not be formed on the surface of the material or that it be difficult for it to form. However, it is frequently extremely difficult to remove ice with a small amount of force once it has formed. In consideration of this fact, it is important to facilitate removal of ice once it has formed. Consequently, there is a desire for an ice attachment preventing agent that has an ice attachment preventing action that includes, in addition to an action of preventing attachment of ice, an action whereby ice that has become attached can be removed extremely simply.

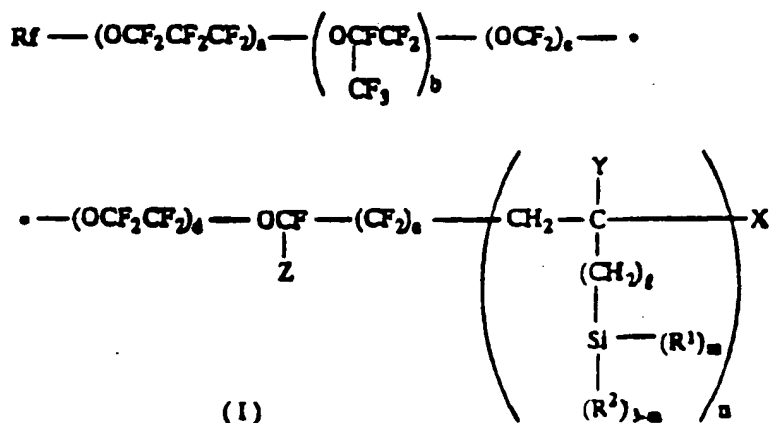
Glass, because of its transparency to light, its heat insulating capacity and its decorative characteristics, is used in a wide range of applications including as a building material for windows of houses, as a material for vehicles such as automobiles and trains and as windshields for ships and aircraft. Glass of this kind is used in places that are in contact with the exterior. It is exposed to rain and is frequently used under conditions in which it is in contact with seawater and polluted water. As in the case of front windshields of automobiles, there are also instances in which assuring visibility is indispensable as a major function. In order to maintain the transparency of glass to light, it is important that the glass itself have the property of repelling water such as rainwater that is attached to it (referred to in the Specification as "water repellency") as a function.

However, in methods in which an organic silicone film is formed on the glass surface, said film is not chemically bonded with the glass. Therefore, there is a high possibility that said film will peel off during use so that it is not of sufficient durability. Further, with methods in which silicon oxide films containing fluoroalkyl groups are formed on the glass surface, durability is sufficient but lubricity and nontackiness are insufficient. For example, when they are used on the front windshields of automobiles, there is the problem that the wiper makes a tearing sound.

Summary of the Invention

The first invention, in the light of the aforementioned present circumstances, has the objective of providing novel silicon-containing fluoropolymers applicable to a wide range of materials and which are of superior resistance to staining.

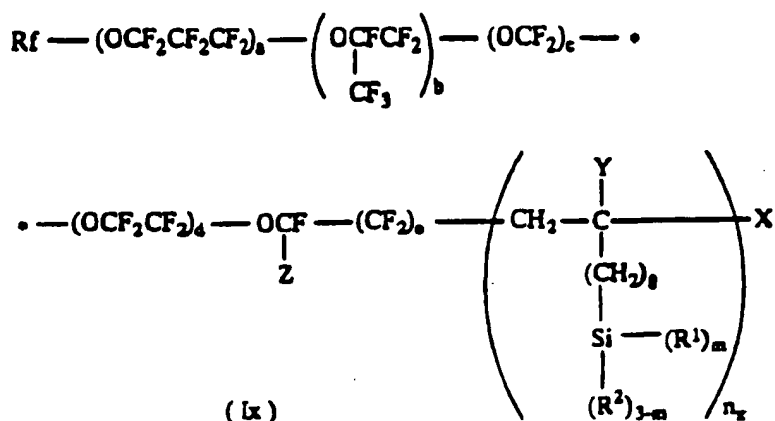
Specifically, The silicon-containing fluoropolymers of this invention are represented by general formula (I)



[wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n indicates an integer of 2 or greater] and have number average molecular weights of 5×10^2 to 1×10^5 .

The second invention, in the light of the aforementioned present circumstances, has the objective of providing a stain preventive base material of superior capacity to prevent staining by oleaginous staining substance, and, in particular, superior capacity to prevent staining by fingerprints.

Specifically, the second invention is a stain preventive base material which forms a layer of organic fluoropolymer containing silicon as represented by general formula (Ix) below and which has a number average molecular weight of 5×10^2 to 1×10^5 on the surface of the base material.



Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.

The third invention, in the light of the aforementioned present circumstances, has the objective of providing a method for the surface treatment of base materials so that there is a sufficient soiling preventive action, so that this action is permanent and so that there is sufficient weather resistance.

Specifically, the third invention is a method of surface treatment of base materials whereby a treatment solution containing (1) an organic fluoropolymer containing silicon as represented by the aforementioned general formula (Ix), (2) an organic solvent containing fluorine and (3) a silane compound [excepting the organic fluoropolymer containing silicone (1) as described above] is applied to the surface of the base material.

The fourth invention, in the light of the aforementioned present circumstances, has the objective of providing a surface treatment composition for base materials having a sufficient soiling preventive action so that this action is permanent and having sufficient weather resistance and which composition is superior from an economic standpoint.

Specifically, the fourth invention is a surface treatment composition which contains (1) an organic fluoropolymer containing silicon as represented by the aforementioned general formula (Ix), (2) an organic solvent containing fluorine and (4) an organic solvent (excepting the organic solvent containing fluorine (2) as described above).

The fifth invention, in the light of the aforementioned present circumstances, has the objective of providing an ice attachment preventive agent that can effectively prevent attachment of ice.

Specifically, the fifth invention is an ice attachment preventive agent that contains an organic fluoropolymer containing silicon as represented by the aforementioned general formula (Ix).

The sixth invention, in the light of the aforementioned present circumstances, has the objective of providing glass of sufficient durability, surface lubricity and surface nontackiness and of superior water repellency.

Specifically, the sixth invention is water repellent glass comprised of a layer of organic fluoropolymer containing silicon as represented by the aforementioned general formula (Ix) formed on the surface of glass.

Detailed Disclosure of the Invention

We shall now present a detailed description of the first invention.

In the formula indicated by the aforementioned general formula (I) which constitutes the organic fluoropolymer containing silicon of this invention, there are no particular limitations on Rf as long as it is a perfluoroalkyl group that ordinarily constitutes organic fluoropolymers. For example, it may be a straight chain or a branched chain substance having 1 to 16 carbon atoms. Preferably, it is CF₃-, C₂F₅- or C₃F₇-.

Z in the aforementioned general formula (I) may be fluorine or it may be a trifluoromethyl group.

The symbols a, b, c, d and e in the aforementioned general formula (I) indicate repeating units of the perfluoropolyether chains that form the main skeleton of the organic fluoropolymers containing silicon of the first invention. They are independent and there are no particular limitations on them as long as they are 0 or integers of 1 or greater and as long as a + b + c + d + e is greater than 1. However, they may be independent and of 0 to 200. When the number average molecular weight of the organic fluoropolymers containing silicon of the first invention to be described subsequently are taken into consideration, they should be, independently, of 0 to 50. The value of a + b + c + d + e should be 1 to 100.

The order of the repeating units parenthesized with subscripts a, b, c, d and e is recorded in the order in the aforementioned general formula (I) for the sake of convenience. In the light of the structure of ordinary perfluoropolyether chains, there are no particular limitations on the order of bonding of these repeating units.

Y in the aforementioned general formula (I) indicates hydrogen or an alkyl group with 1 to 4 carbon atoms. There are no particular limitations in the aforementioned alkyl groups having 1 to 4 carbon atoms. For example, they can be methyl, ethyl, propyl and butyl groups and they may be straight chain or branched chain. X in the aforementioned general formula (I) indicates hydrogen, bromine or iodine. When X is bromine or iodine, the organic fluoropolymer containing silicon is of high radical reactivity, for which reason they can be bonded to other compounds by chemical bonding.

The symbol l in the aforementioned general formula (I) indicates the number of carbon atoms of the alkylene group that is present between the carbon atom of the terminal of the perfluoropolyether chain and the silicon atom that is bonded to it and should be 0, 1 or 2, and, preferably, 0.

The symbol m in the aforementioned general formula (I) indicates the number of bonds of the substituted group R^1 that is bonded to the silicon that is present in the organic fluoropolymer containing silicon of the first invention and is 1, 2 or 3. R^1 is bonded to said silicon in the part in which the substituted group R^1 is not bonded.

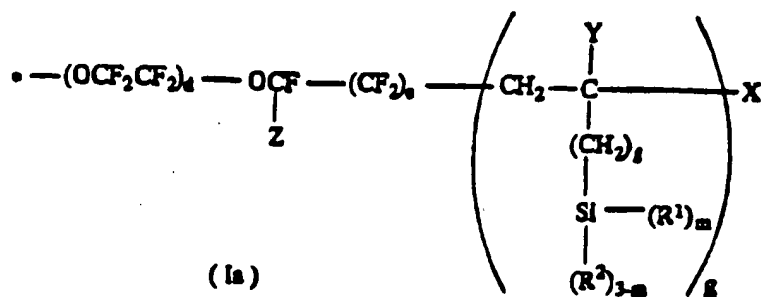
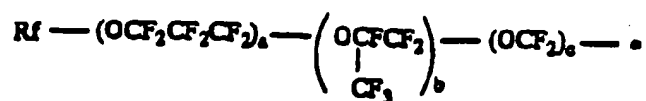
The aforementioned R^1 indicates an hydroxyl group or a hydrolyzable substituted group. There are no particular limitations on the aforementioned hydrolyzable substituted group and it may be, for example, a halogen, $-OR^3$, $-OCOR^3$, $-OC(R^3)=C(R^4)_2$, $-ON=C(R^3)_2$ or $-ON=CR^5$ [wherein, R^3 indicates an aliphatic hydrocarbon group or an aromatic hydrocarbon group, R^4 indicates hydrogen or an aliphatic hydrocarbon group having 1 to 4 carbon atoms and R^5 indicates a divalent aliphatic hydrocarbon group having 3 to 6 carbon atoms]. Preferably, it should be chlorine, $-OCH_3$ or $-OC_2H_5$.

The aforementioned R^2 indicates hydrogen or a monovalent hydrocarbon group. There are no particular limitations on the aforementioned monovalent hydrocarbon groups. Preferably, it can be, for example, a monovalent aliphatic hydrocarbon group, for example, a methyl, ethyl, propyl or a butyl group. It may be straight chain or branched chain.

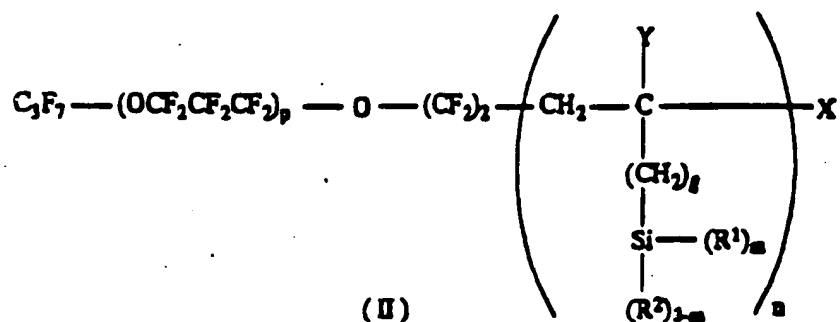
The number average molecular weight of the organic fluoropolymer containing silicon of this invention is 5×10^3 to 1×10^5 . When it is less than 5×10^3 , it does not have properties as a polymer, for which reason it is not usable. When it exceeds 1×10^5 , it lacks processing capacity, for which reasons it is limited to the aforementioned range. Preferably, it should be 1×10^3 to 1×10^4 .

The essential aspect of the first invention lies in the number n in the aforementioned general formula (I). The symbol n in general formula (I) indicates the number of reactive silicon atoms that are contained in the organic fluoropolymer containing silicon of the first invention. In the first invention, n is an integer of 2 or greater. When n is 1 or less, the staining preventive effect, which is the characteristic effect of the first invention, is not sufficient. Therefore, it is limited to 2 or greater. Although there are no particular limitations on the aforementioned n as long as it is 2 or greater, preferably, it should be an integer of 2 to 10.

The organic fluoropolymer containing silicon of the first invention is obtained as a mixture by means of ordinary methods of manufacture. The symbol g in the general formula (Ia) below indicates the number of reactive silicon atoms that are contained in the organic fluoropolymer containing silicon of the first invention which is a mixture. If the mixture of organic fluoropolymers containing silicon of the first invention is 0 or an integer of 1 or greater, the average value of g in the mixture exceeds 1. When the average value of g is less than 1, the staining preventive effect deteriorates when it is used as a staining preventive treatment agent. Preferably, the average value of g should be 1.3 to 3, and, preferably, 1.5 to 2.5.

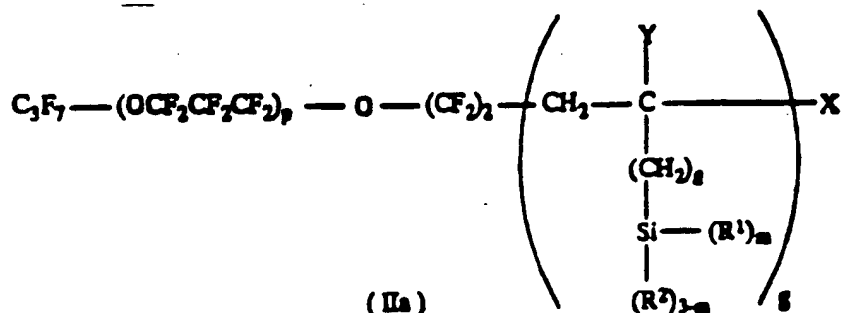


Desirable examples of the organic fluoropolymers containing silicon of the first invention include, for example, substances as indicated by general formula (II) below.



[Wherein, p indicates an integer or 1 or greater and Y, X, R¹, R², l, m and n are the same as described above.]

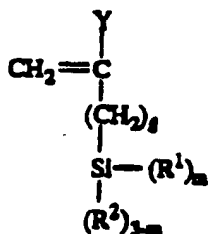
Desirable mixtures of the organic fluoropolymers containing silicon of the first invention can include substances represented, for example, by general formula (IIa) below.



[Wherein, p indicates an integer or 1 or greater and Y, X, R¹, R², l, m and g are the same as described above.]

There are no particular limitations on p in the aforementioned general formula (II) and the aforementioned general formula (IIa) as long as it is an integer of 1 or greater, however, it should be 1 to 200. When the number average molecular weight of the organic fluoropolymers containing silicon of the first invention is taken into consideration, it should be 1 to 50.

The organic fluoropolymer containing silicon of the first invention can be obtained by introducing, for example, iodine into the terminal using perfluoropolyethers that are ordinarily sold commercially as the raw material, after which a vinyl silane compound as indicated, for example, the general formula below [wherein, Y, R¹, R², l and m are the same as indicated previously)] is reacted.



The organic fluoropolymer containing silicon of the first invention can be used as ordinary sealants, sealing agents, paints and coupling agents and for house building materials and automobile parts. They can be used in base materials of optical lenses, eyeglass lenses, glass, metals, ceramics and organic materials for the objective of preventing surface staining.

In using the organic fluoropolymers containing silicon of the first invention, for example, fine powder fillers such as silica, alumina, titanium oxide, carbon and cement, alkoxides of titanium, aluminum and silicon and fine powders of fluorine resins such as other low molecular weight polytetrafluoroethylenes and copolymers of tetrafluoroethylene/hexafluoropropylene can be added as hardness regulators or extending agents. In addition, ordinary cross-linking agents can be added to effect regulation of hardness.

A method in which the aforementioned organic fluoropolymers containing silicon are applied to the surface of the base material can be used for the purpose of forming a layer of the aforementioned organic fluoropolymer containing silicon. The aforementioned application method can be, for example, spray application, spin application, immersion application, roller coating application and gravure application.

Application is facilitated by dilution with a solvent at the time of application. There are no particular limitations on the solvents. For example, they can be a perfluorohexane, a perfluoro-methylcyclohexane, perfluoro-1,1-dimethylcyclohexane and dichloropentafluoropropane (HCFC225).

We shall now present a detailed description of the second invention.

The base materials that serve as the stain preventing base materials of the second invention can be, for example, glass, resin, metals, ceramics, wood, pottery, stone or leather.

There are no particular limitations on the aforementioned glass base material as long as it is formed of various types of glass. For example, it can be used on the surfaces of a show window, a mirror, a water tank, window glass, a dishes shelf or a glass case.

There are no particular limitations on the aforementioned resin material and both natural resins and synthetic resins can be used. The aforementioned natural resins can include, for example, cellulose and lacquer.

The aforementioned synthetic resins can include, for example, polyamide resin, polyacrylate resin, polyamidoimide resin, polyvinyl acetate resin, polyvinyl chloride resin, phenol resin, urea resin, melamine resin, epoxy resin and polyester resin.

There are no particular limitations on the aforementioned metals. They can be, for example, iron, zinc, lead, copper and aluminum.

In the second invention, a layer of organic fluoropolymer containing silicon as represented by the aforementioned general formula (Ix) and having a number average molecular weight of 5×10^3 to 1×10^5 is formed on the surfaces of the aforementioned base materials.

In the formula indicated by general formula (Ix), there are no particular limitations on Rf as long as it is a perfluoroalkyl group that ordinarily forms organic fluoropolymers. For example, it can be a straight chain or branched chain substance having 1 to 16 carbon atoms, and, preferably, CF_3 -, C_2F_5 - or C_6F_{13} -.

Z in the aforementioned general formula (Ix) may be iodine, and, preferably, a trifluoromethyl group.

The symbols a, b, c, d and e in the aforementioned general formula (x) indicate the numbers of repeating units of perfluoropolyether chain that forms the principal skeleton of the organic fluoropolymer containing silicon of the second invention. They are, independently, 0 or integers of 1 or greater. There are no particular limitations as long as $a + b + c + d + e$ is greater than 1. However, independently, it is preferable that they be 0 to 200. When the number average molecular weight of the organic fluoropolymer containing silicon of the second invention, to be described subsequently, is taken into consideration, independently, they should be 0 to 50. The value of $a + b + c + d + e$ should be 1 to 100.

The order of repeating units parenthesized with the subscripts a, b, c, d, and e is, for the sake of convenience, in the order in the aforementioned general formula (Ix). In view of the structure of ordinary perfluoropolyether chains, there are no particular limitations on the bonding order of these repeating units.

Y in the aforementioned general formula (Ix) indicates hydrogen or an alkyl group having 1 to 4 carbon atoms. There are no particular limitations on the alkyl groups having 1 to 4 carbon atoms. For example, they can be methyl, ethyl, propyl or butyl groups and they may be straight chain or branched chain. X in the aforementioned general formula (Ix) indicates, hydrogen, bromine or iodine. When X is bromine or iodine, the radical reactivity of the organic fluoropolymer containing silicon is increased. This is advantageous for bonding with other compounds by chemical bonding.

The symbol l in the aforementioned general formula (Ix) indicates the number of carbon atoms that are present in the alkyl groups between the carbon in the terminal of the perfluoropolyether chain and the silicon that is bonded to it. Its value should be 0, 1 or 2, and, preferably, 0.

The symbol m in the aforementioned general formula (Ix) indicates the number of bonds of the substituted group R¹ that bonds with the silicon that is present in the organic fluoropolymer containing silicon of the second invention. Its value is 1, 2 or 3. R¹ is bonded to said silicon in the portions in which the substituted group R¹ is not bonded.

The aforementioned R¹ indicates an hydroxyl group or a hydrolyzable substituted group. There are no particular limitations on the aforementioned hydrolyzable substituted group. For example, it can be a halogen, $-\text{OR}^1$, $-\text{OCOR}^1$, $-\text{OC}(\text{R}^1)=\text{C}(\text{R}^1)_2$, $-\text{ON}=\text{C}(\text{R}^1)$, or $-\text{ON}=\text{CR}^1$ [wherein, R¹ indicates an aliphatic hydrocarbon group or an aromatic hydrocarbon group, R⁴ indicates hydrogen or an aliphatic hydrocarbon group having 1 to 4 carbon atoms and R⁵ indicates a divalent aliphatic hydrocarbon group having 3 to 6 carbon atoms]. Preferably, it should be chlorine, $-\text{OCH}_3$ or $-\text{OC}_2\text{H}_5$.

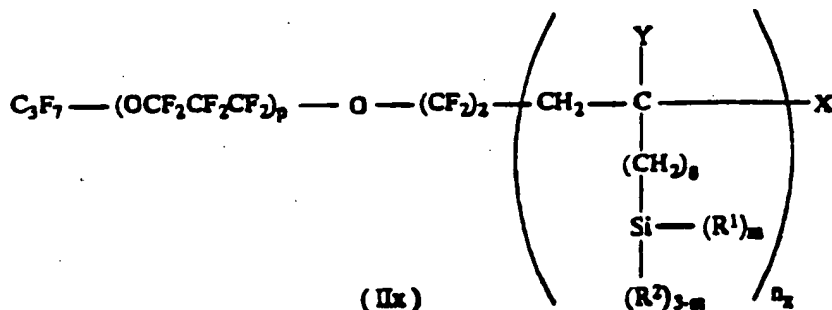
The aforementioned R^1 indicates hydrogen or a monovalent hydrocarbon group. There are no particular limitations on the aforementioned monovalent hydrocarbon group. It may be, for example, a monovalent saturated aliphatic hydrocarbon group, such as, for example, a methyl, ethyl, propyl or butyl group and it may be straight chain or branched chain.

The symbol n_x in the aforementioned general formula (Ix) indicates an integer of 1 or greater. Although there are no particular limitations on it, an integer of 1 to 10 is desirable for the purpose of achieving the objective of the second invention.

The aforementioned n_x indicates an integer in the general formula (Ix). However, the organic fluoropolymer containing silicon of the second invention may also be present as a mixture of polymers indicated by the general formula (Ix) that have the integer n_x . When the organic fluoropolymer containing silicon is present as a mixture of this kind, the aforementioned n_x can be indicated as an average value in said mixture. When said organic fluoropolymer containing silicon is present as a mixture, the average value of n_x , when the objectives of the second invention are taken into consideration, should be 1.3 to 3, and, preferably, 1.5 to 2.5.

The number average molecular weight of the aforementioned organic fluoropolymer containing silicon should be 5×10^3 to 1×10^5 . When it is less than 5×10^3 , it does not have properties as a polymer and it does not have use value. When it exceeds 1×10^5 , it lacks processing capacity. Therefore, it is limited to the aforementioned range. Preferably, it should be 1×10^4 to 1×10^5 .

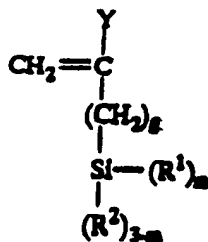
Desirable organic fluoropolymers containing silicon as described above can be, for example, substances as indicated by general formula (IIx) below.



[Wherein, p is an integer of 1 or greater and Y , X , R^1 , R^2 , l , m and n are the same as indicated previously.]

There are no particular limitations on p in the aforementioned general formula (IIx) as long as it is an integer of 1 or greater. However, preferably, it should be 1 to 200. When the number average molecular weight of the organic fluoropolymer containing silicon of the second invention is taken into consideration, it should be 1 to 50.

The aforementioned organic fluoropolymers containing silicon that can be obtained using perfluoropolyethers that are ordinarily sold commercially can be used as raw materials by introducing, for example, iodine, into the terminal and by reacting a vinyl silane compound as indicated by the following general formula [wherein, Y , R^1 , R^2 , l and m are the same as indicated previously] with the product.



In using the aforementioned organic fluoropolymers containing silicon, for example, fine powdered fillers such as silica, alumina, titanium oxide, carbon and cement, alkoxides of titanium, aluminum and silicon, other low molecular weight polytetrafluoroethylenes and fine powders of fluorine resins such as tetrafluoroethylene/hexafluoropropylene copolymers can be added as hardness regulators or extenders. In addition, ordinary cross-linking agents can also be added for regulation of hardness.

In order to form the layer of aforementioned organic fluoropolymer containing silicon, a method can be adopted in which the aforementioned organic fluoropolymer containing silicon is applied to the surface of the base material. There are no particular limitations on the aforementioned application method, and, for example, the method described in the first invention can be used.

At the time of application, dilution with a solvent facilitates application. There are no particular limitations on the solvent, and, for example, the solvents described in the first invention can be used.

There are no particular limitations on the thickness of the layer of organic fluoropolymer containing silicon in the stain preventing base material of the second invention. However, it is desirable that it be 0.001 to 0.03 μ m. When it is less than 0.001 μ m, the stain preventing effect is lacking. When it exceeds 0.03 μ m, the layer is too thick and impediments during use arise. This is not desirable.

Glass products, resin products, metal products and ceramic products that are formed in accordance with the second invention can be used, for example, for parts that are easily stained such as those described below.

Household electrical articles such as the surfaces of the blades of electric fans, of doors of electric ranges and of refrigerators, office articles such as the contrast glass of copy machines, mirrors of OHP units, OHP sheets, keyboards, telephones and office machines, household articles such as glass, doors of food shelves, mirrors, window glass, covers of electric lamps and chandeliers, building materials such as show windows, telephone boxes and water tank glass, vehicle parts such as vehicle glass and painted surfaces of vehicle bodies, personal accessories such as eyeglass frames, glass for underwater eyeglasses, goggles, helmets and glass for covering dials of watches, articles of amusement such as glass for pachinko machines, playing cards and mahjong pieces and coating surfaces of furniture and pianos.

Decorations such as necktie pins, necklaces and earrings, metal or plated products such as water faucets, metal tubular musical instruments, wooden tubular musical instruments, golf clubs, door handles, dumbbells, cutting devices, ceramic materials such as insulators, hygienic porcelain, food utensils and roof tiles, stone materials such as gravestones, checker pieces and marble, paper articles such as wallpaper, sliding screen paper, books, posters and photographs and leather products such as purses, shoes, suitcases, watch bands and baseball gloves.

We shall now present a detailed description of the third invention.

The method of surface treatment of the third invention is characterized in that a treatment solution containing (1) the organic fluoropolymers containing silicon as represented by the aforementioned general formula (Ix), (2) organic solvents

containing fluorine and (3) silane compounds as described in the second invention is applied to the surface of the base material.

The first component of the aforementioned treatment solution is the organic fluoropolymer containing silicon (1) as indicated by the aforementioned general formula (Ix). In the aforementioned general formula (Ix), n_x indicates an integer of 1 or greater. Although there are no particular limitations, an integer of 1 to 10 is preferable for the purpose of achieving the objectives of the third invention.

In the third invention, the aforementioned organic fluoropolymer containing silicon may be present as a mixture of polymers as represented by the aforementioned general formula (Ix). When the aforementioned organic fluoropolymers containing silicon are present as mixtures, the aforementioned n_x can be expressed as an average value in said mixture. When the objectives of the third invention are taken into consideration, the average values of n_x should be 1.3 to 3, and, preferably, 1.5 to 2.5.

The number average molecular weight of the aforementioned organic fluoropolymer containing silicon should be 5×10^3 to 1×10^5 . When it is less than 5×10^3 , the effect of the third invention is not manifested. When it exceeds 1×10^5 , processing capacity is lost. Preferably, it should be 1×10^3 to 1×10^4 .

The second component that forms the aforementioned treatment solution that is used in the surface treatment method of the third invention is the organic solvent containing fluorine (2).

There are no particular limitations on the aforementioned organic solvent containing fluorine (2). For example, it can be a perfluorohexane, a perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane or HCFC225. Of these, HCFC225 is preferable because it easily dissolves the aforementioned organic fluoropolymer containing silicon (1) and because it can easily be acquired.

The third component that forms the aforementioned treatment solution that is used in the surface treatment method of the third invention is the silane compound (3).

There are no particular limitations on the aforementioned compound (3) as long as the aforementioned organic fluoropolymers (1) containing silicon are excepted. For example, it can be an alkoxide compound of silicon as indicated general formula (III) below



(wherein, R^{11} indicates an aliphatic hydrocarbon group, with no particular limitations on the number of carbon atoms) and a partially hydrolyzed condensation product of the compounds indicated by general formula (III). Of these, tetraethoxysilane is preferable because it can easily be acquired.

There are no particular limitations on the component ratios of the components (1), (2) and (3) which constitute the aforementioned treatment solution that is used in the surface treatment method of the third invention. However, it is desirable that the weight ratio of (1) : (2) be 1 : 1 - 1 : 10000. When there is an excess of component (1), the viscosity of the solution increases, for which reason workability is impaired. When there is too little of it, the staining preventing effect is insufficient. Further, the weight ratio of (1) : (3) should be 10 : 1 - 1 : 100. When there is an excess of component (1), the effect in increasing weather resistance is insufficient. When there is too little of it, the staining preventing effect is insufficient. Preferably, it should be 5 : 1 - 1 : 10.

In using the aforementioned treatment solution of the third invention, for example, fine powder additives such as silica, alumina, titanium oxide, carbon and cement, alkoxides such as titanium and aluminum, other low molecular weight polytetrafluoroethylenes and fine powders of fluorine resins such as

tetrafluoroethylene/hexafluoropropylene copolymers can be added as hardness regulators or extenders. In addition, ordinary cross-linking agents, water and hardening catalysts such as hydrochloric acid, sulfuric acid, carboxylic acids and sulfonic acids can be added and hardness regulation can be effected.

In using the aforementioned treatment solution of the third invention, a method in which the aforementioned treatment solution is applied to the surface of the base material as the target can be used. The aforementioned application method can be, for example, brush application, spray coating, spin coating, immersion coating, roller coating, gravure coating and curtain flow coating.

In the surface treatment method of this third invention, there are no particular limitations on the thickness of the layer that is formed by the aforementioned treatment solution. However, it should be $0.001 - 0.03 \mu\text{m}$. When it is less than $0.001 \mu\text{m}$, the staining preventive action is lost. When it exceeds $0.03 \mu\text{m}$, the layer becomes too thick and there are impediments to use. This is not desirable.

In addition to the aforementioned method, the methods described below can be used as the surface treatment method of the third invention.

The treatment solution (M), which contains the organic fluoropolymer containing silicon as indicated by the aforementioned general formula (Ix) and the organic solvent containing fluorine (2) is applied to the surface of the base material, which forms a foundation layer on the surface using a treatment solution (N) containing a silane compound [excepting the organic fluoropolymer containing silicon (1)]. (3).

The aforementioned silane compound (3) is used to form the treatment solution (N) of a specified concentration by means of an organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, ethyl acetate or acetone or water. Although there are no particular limitations on the concentration, it should be in the range of 2 to 80 wt %. When it is less than 2 wt %, a long time is required for formation of the silica sol. When it exceeds 80 wt %, the viscosity of the solution becomes excessive and workability is lost. This is not desirable.

An ordinary catalyst, for example, hydrochloric acid, is added to the aforementioned treatment solution (N), the mixture is allowed to stand for a specified time and a silica sol is formed, after which it was diluted using the aforementioned solvent until a concentration suited to the application operation is dissolved. Although there are no particular limitations on standing time, it is, for example, 2 to 10 days. The dilution concentration differs depending on the thickness of the foundation layer that is desired. For example, it is in the range of 0.2 to 2 wt %.

The diluted treatment solution (N) is applied to the surface of the base material. The application method that can be used includes, for example, brush application, spray coating, spin coating, immersion coating, roller coating, gravure coating and curtain roller coating. A gel layer of a silanol polymer is formed on the surface of the base material by the aforementioned operation.

Next, a foundation layer of which silicon oxide is the principal component can be formed by heating the aforementioned base material. Although the heating temperature differs depending on the base material, it is, for example, in the range of 100 to 300°C . Although there are no particular limitations on heat time, it is, for example, in the range of 10 minutes to 3 hours. Although there are no particular limitations on the thickness of the foundation layers that are formed, it is ordinarily in the range of 0.05 to $0.1 \mu\text{m}$.

Following that, the aforementioned treatment solution (M) is applied to the surface of the base material that forms the foundation layer on the aforementioned surface. The method for application can be, for example, brush application, spray coating, spin coating, immersion coating, roller coating, gravure coating and curtain flow coating.

There are no particular limitations on the thickness of the layer that is formed by the aforementioned treatment solution (M). However, 0.001 to 0.03 μm is desirable. When it is less than 0.001 μm , the staining preventive action is lacking. When it exceeds 0.03 μm , the layer is too thick and there are impediments to use. This is not desirable.

The base materials to which the surface treatment method of the third invention can be applied can be parts that are easily stained such as those indicated below.

Accessories such as necktie pins, necklaces and earrings, metal or plated products such as water faucets, metal tubular musical instruments, wood tubular musical instruments, gold clubs, doorknobs, dumbbells and cutting devices, ceramic materials such as insulators, hygienic porcelain, food utensils and roof tiles, stone materials such as gravestones, checker pieces and marble, paper articles such as wallpaper, sliding screen paper, books, posters and photographs and leather products such as purses, shoes, suitcases, watch bands and baseball gloves.

Household electrical articles such as the surfaces of the blades of electric fans, of doors of electric ranges and of refrigerators, office articles such as the contrast glass of copy machines, mirrors of OHP units, OHP sheets, keyboards, telephones and office machines, household articles such as glass, doors of food shelves, mirrors, window glass, covers of electric lamps and chandeliers, building materials such as show windows, telephone boxes and water tank glass, vehicle parts such as vehicle glass and painted surfaces of vehicle bodies, personal accessories such as eyeglass frames, glass for underwater eyeglasses, goggles, helmets and glass for covering dials of watches, articles of amusement such as glass for pachinko machines, playing cards and mahjong pieces and coating surfaces of furniture and pianos.

The surface treatment method of the third invention is characterized in that the staining preventing action is permanent and in that there is sufficient weather resistance. The materials to which the surface treatment method of the third invention is applicable include, for example, the various base materials indicated below.

Ceramic materials such as doorknobs and roof tile, stone materials such as gravestones, checker pieces and marble, contact glass in copy machines, automobile parts such as vehicle glass and coated surfaces of the vehicle body, articles of amusement such as glass for pachinko machines, playing cards and mahjong pieces.

We shall now present a detailed description of the fourth invention.

The surface treatment composition of the fourth invention contains the organic fluoropolymer containing silicon (1) as represented by the aforementioned general formula (Ix) of the second invention, the fluorine-containing organic solvent (2) and the organic solvent (excepting the fluorine-containing organic solvent (2)) (4).

The first component of the fourth invention is the organic fluoropolymer containing silicon (1) as represented by the aforementioned general formula (Ix). In the aforementioned general formula (Ix), n_1 indicated an integer of 1 or greater. Although there are no particular limitations on it, an integer of 1 to 10 is preferable for the purpose of achieving the objectives of the fourth invention.

In the fourth invention, the aforementioned organic fluoropolymer containing silicon (1) may also be present as a mixture of polymers as represented by the aforementioned general formula (Ix). When it is present as a mixture of organic fluoropolymers containing silicon, the aforementioned n_1 can be expressed as an average value in said mixture. When the objective of the fourth invention is taken into consideration, the average value of n_1 should be 1.3 to 2.5, preferably, 1.5 to 2.5.

The number average molecular weight of the aforementioned fluoropolymer containing silicon (1) should be 5×10^2 to 1×10^5 . When it is less than 5×10^2 , the effect of the fourth invention is not displayed. When it exceeds 1×10^5 , processing capacity is lost. Preferably, it should be 1×10^3 to 1×10^4 .

The second component of the surface treatment composition of the fourth invention is the fluorine-containing organic solvent (2).

There are no particular limitations on the aforementioned fluorine-containing organic solvent (2). For example, it can be any of the substances described in the third invention. Of these, HCFC225 is preferable because it readily dissolves the aforementioned organic fluoropolymer containing silicon (1) and because it can easily be acquired.

The third component of the surface treatment composition of the fourth invention is the organic solvent [excepting the fluorine-containing organic solvent (2)] (4). There are no particular limitations on the organic solvent (4), for example, it can be an alcohol, a ketone, an ester or an halogenated hydrocarbon except for one containing fluorine. Of these, alcohols are preferable.

There are no particular limitations on the aforementioned alcohols. For example, they can be monovalent alcohols with 1 to 8 carbon atoms or polyvalent alcohols such as ethylene glycol and glycerol. Of these, monovalent alcohols with 1 to 4 carbon atoms are preferable and isopropanol is particularly desirable because they can easily be acquired and because they are suited to dissolving the aforementioned silicon-containing organic fluoropolymers (1).

Of the components of the surface treatment composition of the fourth invention, the fluorine-containing organic solvent (2) and the organic solvent (4) function as solvents of the silicon-containing organic fluoropolymer (1). Of the fluorine-containing organic solvent (2) and the organic solvent (4), the fluorine-containing organic solvent (2) is the more expensive and the organic solvent (4) is generally inexpensive. By making the compounding ratio of the organic solvent (4) higher than that of the fluorine-containing organic solvent (2), the surface treatment composition of the fourth invention can be prepared inexpensively.

In the surface treatment composition of the fourth composition, the weight compounding ratio of the fluorine-containing organic solvent (2) and the organic solvent (4), (2) : (4), should be in the range 1 : 99 - 99 : 1. When the ratio of the fluorine-containing organic solvent (2) is less than 1 wt %, the solubility of the fluorine-containing organic fluoropolymer (1) is decreased and the composition does not manifest its function as a surface treatment composition. When it exceeds 99 wt %, a practical cost for the surface treatment composition of this invention cannot be achieved. Preferably, it should be 1 : 99 - 50 : 50.

In using the surface treatment composition of the fourth invention, for example, fine powder additives such as silica, alumina, titanium oxide, carbon and oxides, alkoxides such as titanium and aluminum, other low molecular weight polytetrafluoroethylenes and fine powders of fluorine resins such as tetrafluoroethylene/hexafluoropropylene copolymers can be added as hardness regulators or extenders. In addition, ordinary cross-linking agents, water and hardening catalysts such as hydrochloric acid, sulfuric acid, carboxylic acids and sulfonic acids can be added and hardness regulation can be effected.

In using the aforementioned treatment composition of the fourth invention, a method in which the aforementioned treatment solution is applied to the surface of the base material as the target can be used. There are no particular limitations on the aforementioned application method, and, for example, the methods described for the third invention may be used.

In the fourth invention, a method may be used in which the silicon-containing organic fluoropolymer that has been dissolved by the solvent is applied to a base material surface on the surface of which a foundation layer has been formed in advance by a treatment solution containing a silane compound.

There are no particular limitations on the aforementioned silane compound. For example, it can be the silane compound (3) that is described in the third invention. Of these, tetraethoxysilane is desirable because it can easily be acquired.

The aforementioned silane compound is prepared as a solution of a specified concentration by means of an organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, ethyl acetate and acetone or water. Although there are no particular limitations on the concentration, it is desirable that it be in the range of 2 to 80 wt %. When it is less than 2 wt %, a long time is required for the formation of a silica sol. When it exceeds 80 wt %, its viscosity is excessively increased and workability is lost. This is not desirable.

An ordinary catalyst, for example, hydrochloric acid is added to the aforementioned solution and it is allowed to stand for a specified time to form a silica sol, after which it is diluted using the aforementioned solvents until it reaches a concentration suited to the application operation. Although there are no particular limitations on standing time, it is, for example, 2 to 10 days. Although the dilution concentration differs depending on the desired thickness of the foundation layer, it is, for example, in the range of 0.2 to 2 wt %.

Next, the diluted solution is applied to the surface of the base material. There are no particular limitations on the application method. For example, it can be one of the methods described for the third invention. A gel layer of silanol polymer is formed on the surface of the base material by the aforementioned operation.

Next, a foundation layer of which silicon oxide is the principal component can be formed by heating the aforementioned base material. Although the heating temperature differs depending on the base material, it is, for example, in the range of 100 to 300°C. Although there are no particular limitations on the heating time, it is, for example, in the range of 10 minutes to 3 hours. Although there are no particular limitations on the thickness of the foundation layer that is formed, it is ordinarily in the range of 0.05 to 0.1 μm .

Following that, the silicon-containing organic fluoropolymer, which has been diluted by the aforementioned solvent, is applied to the surface of the base material in the surface of which the foundation layer has been formed. There are no particular limitations on the application method. For example, one of the methods described for the third invention can be used.

Although there are no particular limitations on the thickness of the layer that is formed by the surface treatment composition of the fourth invention, it is desirable for it to be 0.001 to 0.03 μm . When it is less than 0.001 μm , the staining preventive effect is lost. When it exceeds 0.03 μm , the layer becomes too thick and impediments to use arise. This is not desirable.

Base materials to which the surface treatment method of the fourth invention can be applied include, for example, parts that are easily stained as indicated below.

Accessories such as necktie pins, necklaces and earrings, metal or plated products such as water faucets, metal tubular musical instruments, wood tubular musical instruments, gold clubs, bookknobs, dumbbells and cutting devices, ceramic materials such as insulators, hygienic porcelain, food utensils and roof tiles, stone materials such as gravestones, checker pieces and marble, paper articles such as wallpaper, sliding screen paper, books, posters and photographs and leather products such as purses, shoes, suitcases, watch bands and baseball gloves.

Household electrical articles such as the surfaces of the blades of electric fans, of doors of electric ranges and of refrigerators, office articles such as the contrast glass of copy machines, mirrors of OHP units, OHP sheets, keyboards, telephones and office machines, household articles such as glass, doors of food shelves, mirrors, window glass, covers of electric lamps and chandeliers, building materials such as show windows, telephone boxes and water tank glass,

vehicle parts such as vehicle glass and painted surfaces of vehicle bodies, personal accessories such as eyeglass frames, glass for underwater eyeglasses, goggles, helmets and glass for covering dials of watches, articles of amusement such as glass for pachinko machines, playing cards and mahjong pieces and coating surfaces of furniture and pianos.

The surface treatment method of the fourth invention is characterized in that the staining preventing action is permanent and in that the surface treatment composition can easily be prepared. The materials to which the surface treatment method of the third invention is applicable include, for example, the various base materials indicated below.

Household articles such as glass, doors of food shelves, mirrors, window glass, electric lamp shades and chandeliers, building materials such as show windows, telephone boxes and glass for water tanks and automobile parts such as vehicle glass and decorative surfaces of vehicle bodies.

We shall now present a detailed description of the fifth invention.

The icing preventive agent, which is the fifth invention, contains the silicon-containing organic fluoropolymer represented by the aforementioned general formula (Ix) described in the second invention.

In the aforementioned general formula (Ix), n_x indicates an integer of 1 or greater. Although there are no particular limitations on it, it is desirable that it be an integer of 1 to 10 for the purpose of obtaining the objective of the fifth invention.

In the fifth invention, the aforementioned organic fluoropolymer containing silicon (1) may also be present as a mixture of polymers as represented by the aforementioned general formula (Ix). When it is present as a mixture of organic fluoropolymers containing silicon, the aforementioned n_x can be expressed as an average value in said mixture. When the objective of the fifth invention is taken into consideration, the average value of n_x should be 1.3 to 3, and, preferably, 1.5 to 2.5.

The number average molecular weight of the aforementioned fluoropolymer containing silicon (1) should be 5×10^4 to 1×10^5 . When it is less than 5×10^4 , the effect of the fifth invention is not displayed. When it exceeds 1×10^5 , processing capacity is lost. Preferably, it should be 1×10^4 to 1×10^5 .

In using the icing preventive agent of the fifth invention, for example, fine powder additives such as silica, alumina, titanium oxide, carbon and cerent, alkoxides such as titanium and aluminum, other low molecular weight polytetrafluoroethylenes and fine powders of fluorine resins such as tetrafluoroethylene/hexafluoropropylene copolymers can be added as hardness regulators or extenders. In addition, ordinary cross-linking agents, water and hardening catalysts such as hydrochloric acid, sulfuric acid, carboxylic acids and sulfonic acids can be added and hardness regulation can be effected.

In using the icing preventive agent of the fifth invention, a method in which the aforementioned treatment solution is applied to the surface of the base material as the target can be used. There are no particular limitations on the aforementioned application method, and, for example, the methods described for the third invention may be used.

Dilution with a solvent at the time of application facilitates application. There are no particular limitations on these solvents, and, for example, they can be perfluorohexane, perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane and HCFC225.

In the fifth invention, a method may be used in which the silicon containing organic fluoropolymer that has been dissolved by the solvent is applied to a base material surface on the surface of which a foundation layer has been formed in advance by a treatment solution containing a silane compound.

There are no particular limitations on the aforementioned silane compound. For example, it can be the silane compound (3) that is described in the third invention. Of these, tetraethoxysilane is desirable because it can easily be acquired.

The aforementioned silane compound is prepared as a solution of a specified concentration by means of an organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, ethyl acetate and acetone or water. Although there are no particular limitations on the concentration, it is desirable that it be in the range of 2 to 80 wt %. When it is less than 2 wt %, a long time is required for the formation of a silica sol. When it exceeds 80 wt %, its viscosity is excessively increased and workability is lost. This is not desirable.

An ordinary catalyst, for example, hydrochloric acid is added to the aforementioned solution and it is allowed to stand for a specified time to form a silica sol, after which it is diluted using the aforementioned solvents until it reaches a concentration suited to the application operation. Although there are no particular limitations on standing time, it is, for example, 2 to 10 days. Although the dilution concentration differs depending on the desired thickness of the foundation layer, it is, for example, in the range of 0.2 to 2 wt %.

Next, the diluted solution is applied to the surface of the base material. There are no particular limitations on the application method. For example, it can be one of the methods described for the third invention. A gel layer of silanol polymer is formed on the surface of the base material by the aforementioned operation.

Next, a foundation layer of which silicon oxide is the principal component can be formed by heating the aforementioned base material. Although the heating temperature differs depending on the base material, it is, for example, in the range of 100 to 300°C. Although there are no particular limitations on the heating time, it is, for example, in the range of 10 minutes to 3 hours. Although there are no particular limitations on the thickness of the foundation layer that is formed, it is ordinarily in the range of 0.05 to 0.1 μm .

Following that, the silicon-containing organic fluoropolymer, which has been diluted by the aforementioned solvent, is applied to the surface of the base material in the surface of which the foundation layer has been formed. There are no particular limitations on the application method. For example, one of the methods described for the third invention can be used.

Although there are no particular limitations on the thickness of the layer that is formed by the icing preventive agent of the fifth invention, it is desirable for it to be 0.001 to 0.03 μm . When it is less than 0.001 μm , the icing preventive effect is lost. When it exceeds 0.03 μm , the layer becomes too thick and impediments to use arise. This is not desirable.

There are no particular limitations on the base materials to which the icing preventive agent of the fifth invention can be applied. For example, they can include vehicles such as automobiles and trains, moving objects such as aircraft and ships, base materials that are used in building material for houses, special facilities such as freezing test equipment and household electrical articles such as refrigerators. Of these, it is particularly important as windshield glass for vehicles, aircraft and ships because of the dangers that arise due to icing.

We shall now present a detailed description of the sixth invention.

The water repellent glass which is the sixth invention consists of a layer of the silicon-containing fluoropolymer as represented by the aforementioned general formula (Ix) as described in the second invention formed on the surface of glass.

In the aforementioned general formula (Ix), n , indicates an integer of 1 or greater. Although there are no particular limitations on it, it is desirable

that it be an integer of 1 to 10 for the purpose of obtaining the objective of the fifth invention.

In the sixth invention, the aforementioned organic fluoropolymer containing silicon (1) may also be present as a mixture of polymers as represented by the aforementioned general formula (I_x). When it is present as a mixture of organic fluoropolymers containing silicon, the aforementioned n_x can be expressed as an average value in said mixture. When the objective of the sixth invention is taken into consideration, the average value of n_x should be 1.3 to 3, and, preferably, 1.5 to 2.5.

The number average molecular weight of the aforementioned fluoropolymer containing silicon (1) should be 5×10^2 to 1×10^5 . When it is less than 5×10^2 , the effect of the sixth invention is not displayed. When it exceeds 1×10^5 , processing capacity is lost. Preferably, it should be 1×10^3 to 1×10^4 .

In using the aforementioned silicon-containing organic fluoropolymer, for example, fine powder additives such as silica, alumina, titanium oxide, carbon and cement, alkoxides such as titanium and aluminum, other low molecular weight polytetrafluoroethylenes and fine powders of fluorine resins such as tetrafluoroethylene/hexafluoropropylene copolymers can be added as hardness regulators or extenders. In addition, ordinary cross-linking agents, water and hardening catalysts such as hydrochloric acid, sulfuric acid, carboxylic acids and sulfonic acids can be added and hardness regulation can be effected.

The method for applying the aforementioned silicon-containing organic fluoropolymer to the surface of glass can be used to form the layer of the aforementioned silicon-containing organic fluoropolymer. There are no particular limitations on the aforementioned application method. For example, the substances described for the third invention can be used.

Dilution with a solvent at the time of application facilitates application. There are no particular limitations on these solvents, and, for example, those described in the third invention can be used.

In the sixth invention, a method may be used in which the silicon containing organic fluoropolymer that has been dissolved by the solvent is applied to a base material surface on the surface of which a foundation layer has been formed in advance by a treatment solution containing a silane compound.

There are no particular limitations on the aforementioned silane compound. For example, it can be the silane compound (3) that is described in the third invention. Of these, tetraethoxysilane is desirable because it can easily be acquired.

The aforementioned silane compound is prepared as a solution of a specified concentration by means of an organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, ethyl acetate and acetone or water. Although there are no particular limitations on the concentration, it is desirable that it be in the range of 2 to 80 wt %. When it is less than 2 wt %, a long time is required for the formation of a silica sol. When it exceeds 80 wt %, its viscosity is excessively increased and workability is lost. This is not desirable.

An ordinary catalyst, for example, hydrochloric acid is added to the aforementioned solution and it is allowed to stand for a specified time to form a silica sol, after which it is diluted using the aforementioned solvents until it reaches a concentration suited to the application operation. Although there are no particular limitations on standing time, it is, for example, 2 to 10 days. Although the dilution concentration differs depending on the desired thickness of the foundation layer, it is, for example, in the range of 0.2 to 2 wt %.

Next, the diluted solution is applied to the surface of the base material. There are no particular limitations on the application method. For example, it can be one of the methods described for the third invention. A gel layer of silanol polymer is formed on the surface of the base material by the aforementioned operation.

Next, a foundation layer of which silicon oxide is the principal component can be formed by heating the aforementioned base material. Although the heating temperature differs depending on the base material, it is, for example, in the range of 100 to 300°C. Although there are no particular limitations on the heating time, it is, for example, in the range of 10 minutes to 3 hours. Although there are no particular limitations on the thickness of the foundation layer that is formed, it is ordinarily in the range of 0.05 to 0.1 μm .

Following that, the silicon-containing organic fluoropolymer, which has been diluted by the aforementioned solvent, is applied to the surface of the base material in the surface of which the foundation layer has been formed. There are no particular limitations on the application method. For example, one of the methods described for the third invention can be used.

Although there are no particular limitations on the thickness of the silicon-containing organic fluoropolymer layer on the water repellent glass which is the sixth invention, it is desirable for it to be 0.001 to 0.03 μm . When it is less than 0.001 μm , the water repellent effect is lost. When it exceeds 0.03 μm , the layer becomes too thick and impediments to use arise. This is not desirable.

Optimum Mode for Executing the Invention

We shall now present a more detailed description of this invention by presenting examples and comparative examples. However, this invention is not limited by these examples.

Example of Synthesis 1

2617 g (10.3 mol) of iodine, 213.2 g (1.54 mol) of potassium carbonate and 9000 g of hexachloro-1,3-butadiene were introduced into a 2.0 liter four-neck flask equipped with a stirrer, a dropping funnel, a reflux condenser and a thermometer and 4000 g (1.03 mol) of ω -fluoropolyperfluorooxetane acyl fluoride (average molecular weight, 3900) as represented by the chemical formula $\text{F}-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_n-\text{CF}_2\text{CF}_2\text{COF}$ was added dropwise at a rate of 10 mL/minute in a nitrogen gas flow as the temperature of the system was being maintained at 160°C.

After the dropwise addition was completed, the reaction temperature was raised to 185°C and a reaction was carried out for 20 hours.

After the reaction was completed, the system was cooled, after which the potassium salt was separated by filtration and the bottom layer was collected from the liquid phase, which was separated into two layers, using a separating funnel. It was washed several times using acetone, after which it was dissolved in 1 liter of perfluorohexane and the fine insoluble matter was separated by filtration with a glass filter. 3890 g (yield, 95%) of ω -fluoropolyperfluorooxetane iodine compound as represented by the chemical formula $\text{F}-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_n-\text{CF}_2\text{CF}_2\text{I}$ was obtained by completely removing the volatile matter under decreased pressure from the solution obtained.

From the infrared absorption spectrum, it can be seen that absorption of CF_2I at 1890 cm^{-1} was completely lost and that there was a new absorption band of CF_2I at 910 cm^{-1} .

Example of Synthesis 2

A substance comprised of 40 g of the ω -fluoropolyperfluorooxetane iodine compound as represented by the chemical formula $\text{F}-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_n-\text{CF}_2\text{CF}_2\text{I}$ that was synthesized in Example of Synthesis 1 dissolved in 30 g of hexafluorotetrachloroethane [Daiflon (phonetic)* Sorbent S-316 manufactured by Daikin Kogyo Company] and of 1.5 g (1×10^{-2} mol) of di-*t*-butyl peroxide was introduced into a 200 mL four-neck flask equipped with a stirrer, a dropping funnel, a reflux condenser and a thermometer and the atmosphere in the system was completely replaced by nitrogen. After which 16.1 g (0.10 mol) of vinyl trichlorosilane was added dropwise by means of a dropping funnel in a nitrogen gas flow. After the dropwise addition

*Translator's note: Transliterated phonetically from the Japanese. As such, the spelling may differ from other transliterations.

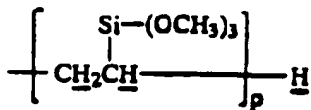
was completed, 38.7 g (yield, 90%) of silicon-containing organic fluoropolymer (A) having iodine in the terminal was obtained by completely removing the volatile matter under reduced pressure.

Example of Synthesis 3

A substance consisting of 34.4 g (8×10^{-3} mol) of the silicon-containing organic fluoropolymer (A) that was synthesized in Examples of Synthesis 2 dissolved in 50 g of perfluorohexane was introduced into a 200 ml four-neck flask equipped with a stirrer, a dropping funnel, a reflux condenser and a thermometer and 2.1 g (3.2×10^{-2} mol) was dispersed by forceful stirring. The system was cooled in an ice water bath and 10 g of anhydrous methanol was added dropwise in a nitrogen gas flow.

After the dropwise addition was completed, the ice water bath was removed and a reaction was carried out for 2 hours under heating and reflux. After the reaction was completed, the insoluble matter was separated by filtration and the bottom layer was collected using a separating funnel from the liquid phase, which had separated into two layers. The solution that was obtained was washed 3 times using anhydrous methanol, after which 31.6 g (yield, 92%) of silicon-containing organic fluoropolymer (B) was obtained by completely removing the volatile matter under reduced pressure.

A broad absorbing moiety originating from the hydrogen atoms in the formula indicated below was manifested at 1.2 to 3.0 ppm by $^1\text{H-NMR}$. 5.0 mol % of ω -fluoroperfluorooxetane hydride was added as an internal standard and the degree of polymerization was calculated by the equation indicated below. It was found to be 2.0.



$$I/I_s = [0.95 (3P + 1)] / 0.05$$

I : integrated absorption intensity of 1.2 to 3.0 ppm

I_s : integrated absorption intensity of the internal standard

P : degree of polymerization

Example of Synthesis 4

When synthesis was performed in the same way as in Example of Synthesis 2 except that 0.29 g (2×10^{-3} mol) of di-*t*-butyl peroxide was used, the silicon-containing organic fluoropolymer (C) was obtained.

Example of Synthesis 5

Synthesis was performed in the same way as in Example of Synthesis 3 except that the silicon-containing organic fluoropolymer (C) was used as the raw material. When the degree of polymerization of the silicon-containing fluoropolymer that was obtained was calculated in the same way as in Example of Synthesis 3, it was 1.0.

Example 1 and Comparative Examples 1 and 2

Treatment solutions were prepared comprised of 0.1 wt % perfluorohexane solutions of the substances obtained in Examples of Synthesis 3 and 5 and commercially available silica coupling agent containing fluorine KBM7803 ($\text{C}_6\text{F}_{11}\text{CH}_2\text{CH}_2\text{Si}(\text{OH})_3$) manufactured by the Shin-Etsu Chemical Company (hereafter referred to simply as "commercial product"). A glass plate, which served as the base material, was washed with water before use, after which it was washed thoroughly with ethanol and acetone. The glass plate, which had been prepared in this way, was dipped for 10 seconds in the treatment solution and was air-dried for 60 minutes after it was removed. Next, it was subjected to ultrasonic washing for 5 minutes in perfluorohexane, the excess treatment agent molecules were removed and it was air-dried. Determinations were made of the product.

The evaluations were performed by the following standards.

- (1) Thumbprint attachment characteristics were evaluated by applying thumbprints to the test material and assessing ease of attachment by visual observation.
 - O: Few thumbprints were attached and attached thumbprints were not conspicuous
 - X: Same degree of attachment of thumbprints as on an untreated glass plate
 - Δ: Hard to determine either of the above
- (2) Thumbprint wiping off characteristics were evaluated by wiping the surface of the test material used for evaluation of thumbprint attachment characteristics back and forth with Kim Wipe (manufactured by Jujo Kimberly Company) and by assessing the ease with which the fingerprints were wiped off by visual observation.
 - O: Fingerprints could be completely wiped off
 - Δ: Wipe-off traces of fingerprints remained
 - X: There were widespread wipe-off traces of fingerprints and they were difficult to remove
- (3) Determination of the angle of contact with water was determined using an angle of contact meter (Model CA-DT, manufactured by the Kyowa Kaimen Kagaku Kikai [Kyowa Interface Scientific Machines] Company).

The results of the evaluations are shown in Table 1.

Table 1

	Evaluated sample	Fingerprint attachment characteristics	Fingerprint wiping off characteristics	Angle of contact with water
Example 1	Example of Synthesis 3	O	O	113°
Comparative Example 1	Example of Synthesis 5	Δ	O	113°
Comparative Example 2	Commercial product	Δ	X	111°

Example 2 and Comparative Example 3

Treatment solutions were prepared comprised of 0.1 wt % perfluorohexane solutions of the substance obtained in Example of Synthesis 3 and of the commercial product. An aluminum plate that served as the based material [a 0.5 mm plating] as stipulated in JIS H4000 (A1050P) was washed with water before use, after which it was washed thoroughly using methanol and acetone. The aluminum plate that had been prepared in this way was dipped for 10 seconds in the treatment solution and was air-dried for 60 minutes after it had been removed. Next, it was subjected to ultrasonic washing for 5 minutes in perfluorohexane, the excess treatment molecules were removed and the plate was air-dried for use in determinations.

Comparative Example 4

A separate untreated aluminum plate was prepared.

The evaluations were made by the following standards.

The surface of the test material and a Kim Wipe (manufactured by Jujo Kimberly Company) were held in the hands and the surface was wiped back and forth repeatedly 100 times with a force of medium strength. Determinations were made of the angle of contact with the water before the wiping operation and of the angle of contact with the water after the wiping operation. The determinations of angle of contact with water were made using an angle of contact meter (Model CA-DT, manufactured by the Kyowa Kaimen Kagaku Kikai Company).

Table 2 shows the results of these evaluations.

[Table 2]

	Evaluated sample	Angle of contact with water before the procedure	Angle of contact with water after the procedure
Example 2	Example of Synthesis 3	114°	108°
Comparative Example 3	Commercial product	111°	98°
Comparative Example 4	Untreated plate	88°	--

Example 3

99.8 wt % of HCFC225 and 0.1 wt % tetraethoxysilane were mixed with 0.1 wt % of the silicon-containing fluoropolymer (B) obtained in Example of Synthesis 3, with a treatment solution being prepared.

A glass plate was washed with water before use, after which it was washed thoroughly using methanol and acetone. The glass plate that had been prepared in this way was dipped for 1 minute in the treatment solution, and, after removal, was allowed to stand for 60 minutes at 60°C and 80% RH. Next, it was washed thoroughly with HCFC225 and the excess treatment solution molecules were removed.

The test specimen that was made in this way was subjected to an accelerated weather resistance test with an Ai Super UV tester (SUV-W13, manufactured by Iwasaki Denki Company) and the angles of contact with water before and after the test were compared. The angle of contact with water was determined using an angle of contact meter (Model; CA-DT, manufactured by the Kyowa Kaimen Kagaku Kikai Company). The results are shown in Table 3.

Comparative Example 5

A treatment solution was prepared in the same way as in Example 3 except that the treatment solution was prepared by mixing 99.9 wt % of HCFC225 with 0.1 wt % of the silicon-containing organic fluoropolymer (B) obtained in Example of Synthesis 3 and similar tests were performed.

Table 3

	Angle of contact with water	
	Before test	After test
Example 3	114°	109°
Comparative Example 5	112°	101°

Example 4

A surface treatment composition was obtained by mixing 0.1 wt % of the silicon-containing organic fluoropolymer (B) with 99.9 wt % of mixed solvent comprised of 10 wt % of HCFC225 and 90 wt % of isopropanol.

A glass plate was washed with water before use, after which it was washed thoroughly using methanol and acetone. The glass plate that had been prepared in this way was dipped for 1 minute in the aforementioned surface treatment composition, and, after removal, was allowed to stand for 24 hours at 60°C and 90% RH. Next, it was washed thoroughly with HCFC225 and the excess surface treatment composition molecules were removed.

Comparative Example 6

A treatment solution was prepared in the same way as in Example 4 except that the surface treatment composition was prepared by mixing 99.9 wt % of HCFC225 with 0.1 wt % of the silicon-containing organic fluoropolymer (B) and similar tests were performed. The results are shown in Table 4.

Table 4

Test sample	Angle of contact with water
Example 4	113°
Comparative Example 6	113°

Comparative Example 7

An attempt was made to prepare a surface treatment composition by mixing 0.1 wt % of the silicon-containing organic fluoropolymer (B) with 99.9 wt % of isopropanol. However, the two substances did not mix and a surface treatment composition could not be obtained.

Example 5

A treatment solution was prepared comprised an 0.1 wt % perfluorohexane solution of the substance obtained in Example of Synthesis 3. A glass plate was washed with water before use, after which it was thoroughly washed using methanol and acetone. The glass plate that had been prepared in this way was dipped for 10 seconds in the treatment solution, and, after it was removed, it was air-dried for 60 minutes. Next, it was subjected to ultrasonic washing for 5 minutes in perfluorohexane, the excess treatment agent molecules were removed and it was air-dried.

The treated glass plate was allowed to stand on dry ice in an atmosphere at 10°C and 70% RH, with icing of a thickness of approximately 0.2 mm being produced.

The glass plate surface that had undergone icing was wiped gently back and forth several times using a spatula made of polyethylene and the icing preventive effect was evaluated based on removal of the icing. The standards of evaluation were as follows.

- O: The icing could easily be wiped off and the entire surface of the glass could be exposed
- Δ: The glass surface could be exposed but icing remained in places
- X: The glass surface was not exposed

The results are shown in Table 5.

Comparative Example 8

A treatment solution was prepared comprised an 0.1 wt % perfluorohexane solution of the commercial product. A glass plate was washed with water before use, after which it was thoroughly washed using methanol and acetone. The glass plate that had been prepared in this way was dipped for 10 seconds in the treatment solution, and, after it was removed, it was air-dried for 60 minutes. Next, it was subjected to ultrasonic washing for 5 minutes in perfluorohexane, the excess treatment agent molecules were removed and it was air-dried.

The treated glass plate was allowed to stand on dry ice in an atmosphere at 20°C and 70% RH, with icing of a thickness of approximately 0.2 mm being produced.

Evaluations of icing preventive effect were performed in the same way as in Example 5. The results are shown in Table 5.

Comparative Example 9

A glass plate that had been washed with water before use and that after that had been thoroughly washed using methanol and acetone was allowed to stand on dry ice in an atmosphere at 20°C and 70% RH, with icing of approximately 0.2 mm in thickness being produced.

Evaluation of the icing preventive effect was performed in the same way as in Example 5. The results are shown in Table 5.

Table 5

	Evaluated test sample	Evaluation
Example 5	Example of Synthesis 3	O
Comparative Example 8	Commercial product	Δ
Comparative Example 9	--	X

Example 6 and Comparative Example 10

Treatment solutions were prepared of 0.1 wt % perfluorohexane solutions of the substance obtained in Example of Synthesis 3 and of the commercial product. A glass plate was washed with water before use, after which it was thoroughly washed using methanol and acetone. The glass plate that had been prepared in this way was dipped for 10 seconds into the treatment solution. After it was removed, it was air-dried for 60 minutes. Next, it was subjected to ultrasonic washing for 5 minutes in perfluorohexane, the excess treatment agent molecules were removed and it was air-dried and used for determinations.

The angle of contact with water and the water droplet falling angle were determined using an angle of contact meter (Model CA-DT manufactured by the Kyowa Kaimen Kagaku Kikai Company).

Peeling strength was determined using commercial cellophane tape (18 mm in width; manufactured by Sekisui Chemical Industrial Company) at a peeling speed of 50 mm/second.

Table 6

	Evaluated Sample	Angle of contact with water	Water droplet falling angle	Peeling strength
Examples 6	Example of Synthesis 3	111°	14°	123 :
Comparative Example 10	Commercial product	110°	30°	213 :

Possibility of Industrial Use

Because the fluorine-containing polymer which is the first invention is of the structure described above, it has extremely good staining preventing capacity against fingerprints and angle of contact with water and can be applied to a wide range of fields such as optical lenses, eyeglass lenses, glass, metals, ceramics and organic materials.

Because the staining preventive base material which is the second invention is of the structure described above, it has extremely good staining preventing capacity against fingerprints and can be used for such base materials as glass, resins, metals, ceramics, wood, porcelain, stone and leather.

Because the surface treatment method which is the third invention is of the structure described above, it has a sufficient staining preventive action; its action is permanent, it also has sufficient weather resistance and can be used suitably as a base material when a staining preventive action is required under harsh conditions such as outdoor exposure.

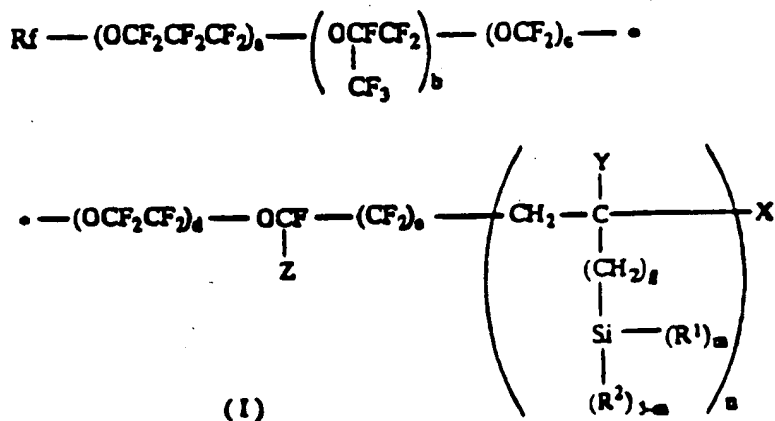
Because the surface treatment composition which is the fourth invention is of the structure described above, it has a sufficient staining preventive action, its action is permanent, it also has sufficient weather resistance and can be obtained inexpensively, for which reason it is widely used.

Because the icing preventive agent which is the fifth invention is of the structure described above, it can effectively prevent attachment of ice and can remove ice extremely easily once it has become attached.

Because the water repellent glass which is the sixth invention is of the structure described above, it is of superior durability, surface lubricity and surface nonadhesiveness and also has sufficient water repellency, for which reason it can be used suitable as windshield glass for buildings, vehicles, ships and aircraft.

Claims

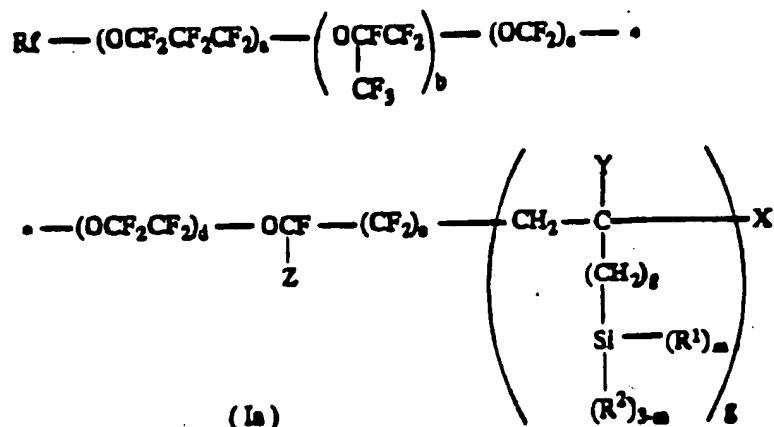
1. A silicon-containing organic fluoropolymer characterized in that it is represented by general formula (I):



[wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in

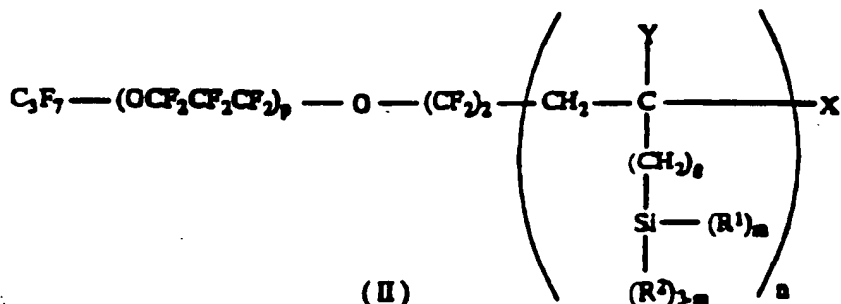
the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R^1 indicates a hydroxyl group or a hydrolyzable substituted group, R^2 indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n indicates an integer of 2 or greater] and in that its number average molecular weight is 5×10^3 to 1×10^5 .

2. A mixture of silicon-containing organic fluoropolymers characterized in that it is represented by general formula (Ia):



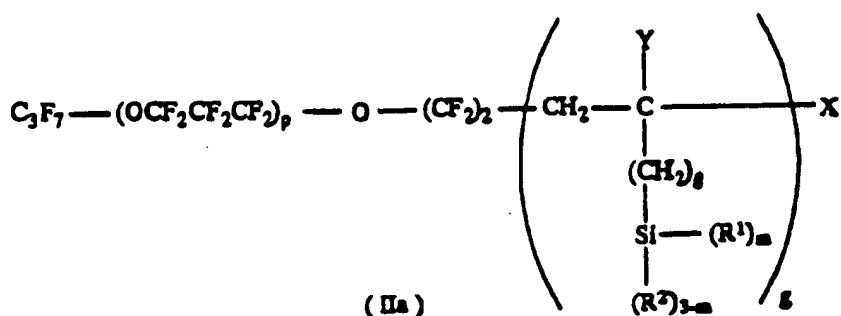
[wherein, R_f indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R^1 indicates a hydroxyl group or a hydrolyzable substituted group, R^2 indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2 and m indicates 1, 2 or 3] in that it is a silicon-containing organic fluoropolymer of which the number average molecular weight is 5×10^3 to 1×10^5 , in that it is a mixture of substances in which g is 0 or an integer of 1 or greater and in which the average value of the aforementioned g exceeds 1.

3. A silicon-containing organic fluoropolymer as described in Claim 1 characterized in that the silicon-containing fluoropolymer is represented by general formula (II)



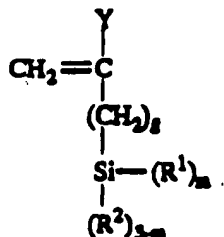
[wherein, p indicates an integer of 1 or greater, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n indicates an integer of 2 or greater] and in that its number average molecular weight is 5×10^2 to 1×10^5 .

4. A mixture of silicon-containing organic fluoropolymers characterized in that it is represented by general formula (IIa):

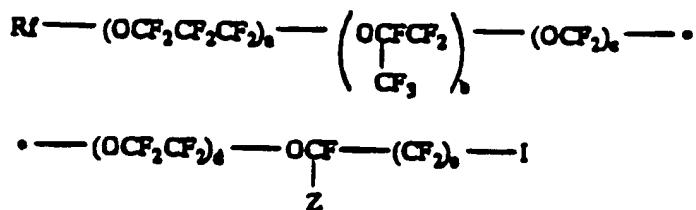


[wherein, p indicates an integer of 1 or greater, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, and m indicates 1, 2 or 3], in that it is a silicon-containing organic fluoropolymer of which the number average molecular weight is 5×10^2 to 1×10^5 , in that it is a mixture of substances in which g is 0 or an integer of 1 or greater and in which the average value of the aforementioned g exceeds 1.

5. A method for the manufacture of silicon-containing organic fluoropolymers as described in Claim 1 characterized in that a vinyl silane compound as indicated by the general formula



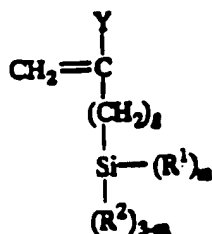
[wherein, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, R^1 indicates a hydroxyl group or a hydrolyzable substituted group, R^2 indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, and m indicates 1, 2 or 3] is reacted with an organic fluoropolymer into the terminal of which iodine has been introduced as indicated by the general formula



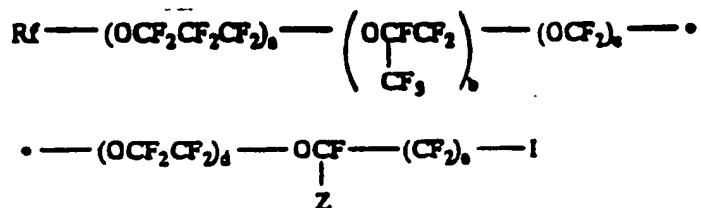
[wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order :

repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula].

6. A method for the manufacture of a mixture of silicon-containing organic fluoropolymers as described in Claim 2 characterized in that a vinyl silane compound as indicated by the general formula

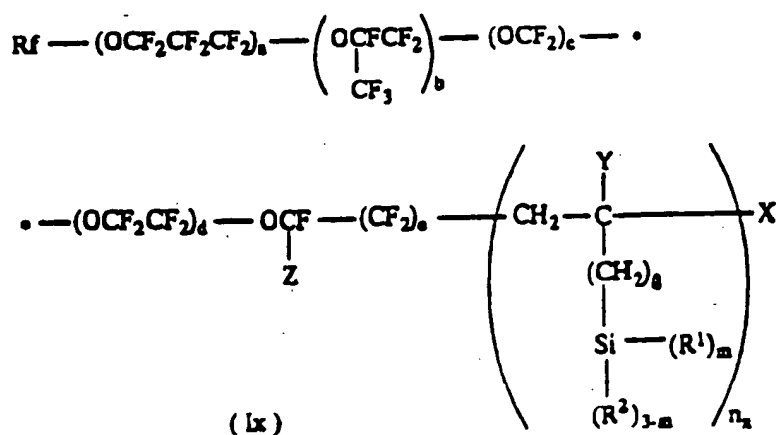


[wherein, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, b indicates 0, 1 or 2, and m indicates 1, 2 or 3] is reacted with an organic fluoropolymer into the terminal of which iodine has been introduced as indicated by the general formula



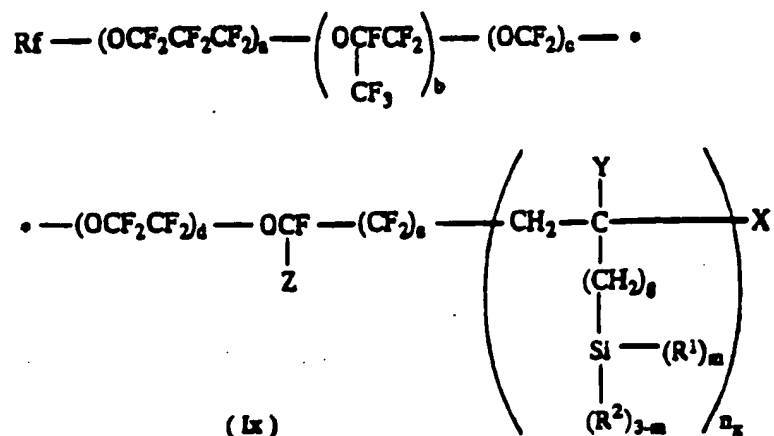
[wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula].

7. A staining preventive base material characterized in that it forms a layer of silicon organic fluoropolymer that is represented by general formula (Ix) below and that has a number average molecular weight of 5×10^4 to 1×10^5 on the surface of the base material.



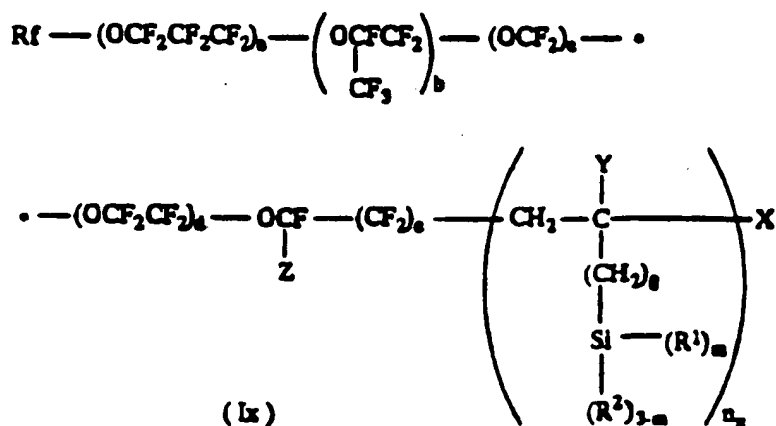
[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, m indicates 0, 1 or 2, m indicates 1, 2 or 3 and n₁ indicates an integer of 1 or greater.]

8. A surface treatment method characterized in that a treatment solution containing the silicon-containing fluoropolymer (1) as indicated by general formula (Ix) below, a fluorine containing solvent (2) and a silane compound [excepting the aforementioned silicon-containing fluoropolymer (1)] (3).



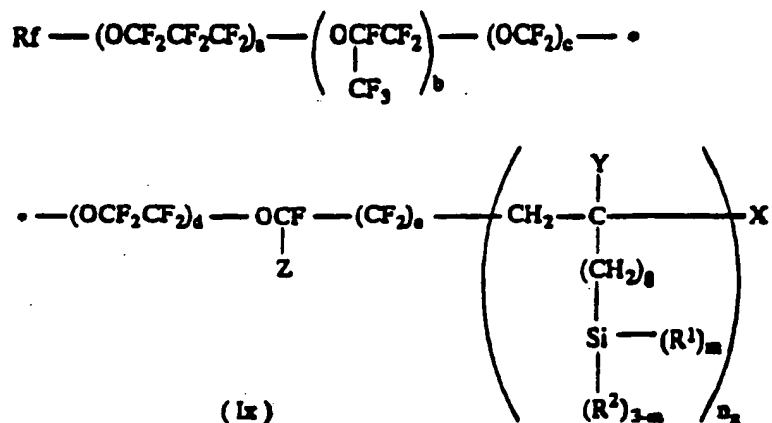
[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, $a + b + c + d + e$ is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R^1 indicates a hydroxyl group or a hydrolyzable substituted group, R^2 indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.] is applied to the surface of the base material.

9. A surface treatment method characterized in that a treatment solution (N) that contains the silane compound [excepting the silicon-containing fluoropolymer (1) as indicated by general formula (Ix) below] (3) is applied to the surface of the base material to form a foundation layer, after which the treatment solution (M) which contains the aforementioned silicon-containing organic fluoropolymer (1) and the fluorine-containing organic solvent (2) is applied to the aforementioned foundation layer.



[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.]

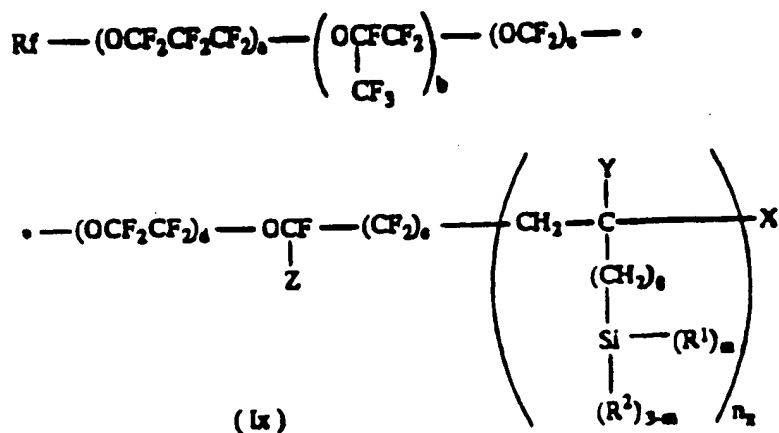
10. A surface treatment composition characterized in that it contains the silicon-containing organic fluoropolymer (1) as indicated by general formula (1x) below, the fluorine-containing organic solvent (2) and the organic solvent [excepting the fluorine-containing organic solvent (2)] (4).



[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.]

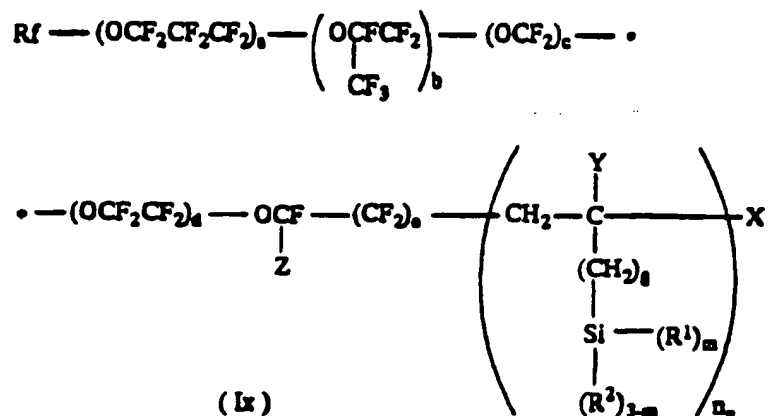
11. A surface treatment composition as described in Claim 10 in which the organic solvent is an alcohol [excepting the fluorine-containing organic solvent (2)] (4).

12. An icing preventive agent characterized in that it contains the silicon-containing organic fluoropolymer indicated by general formula (1x) below.



[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.]

13. Water repellent glass characterized in that a layer of silicon-containing organic fluoropolymer as indicated by general formula (Ix) below is formed on the surface of glass.



[Wherein, Rf indicates a perfluoroalkyl group, Z indicates fluorine or a trifluoromethyl group, a, b, c, d, and e, independently, indicate 0 or an integer of 1 or greater, a + b + c + d + e is at least 1 or greater, the order of repeating units parenthesized with subscripts a, b, c, d and e is not limited in the formula, Y indicates hydrogen or an alkyl group with 1 to 4 carbon atoms, X indicates hydrogen, bromine or iodine, R¹ indicates a hydroxyl group or a hydrolyzable substituted group, R² indicates a monovalent hydrocarbon group, l indicates 0, 1 or 2, m indicates 1, 2 or 3 and n_x indicates an integer of 1 or greater.]

14. Water repellent glass as described in Claim 13 in which the water repellent glass is used in vehicles.